Pergamon

Tetrahedron Letters 43 (2002) 5333–5337

TETRAHEDRON LETTERS

Novel ether-ring transformation via a phenonium ion

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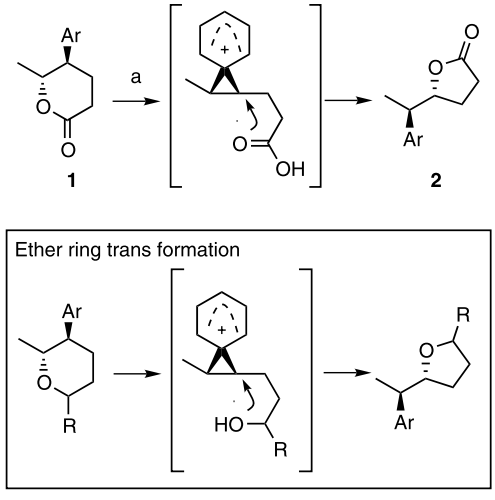
Received 11 April 2002; revised 20 May 2002; accepted 24 May 2002

Abstract—Upon treatment with CF_3COOH at 70°C, trisubstituted-tetrahydropyrans, which were stereoselectively prepared from δ-lactones, were found to be converted into the corresponding 2,5-disubstituted-tetrahydrofurans stereospecifically via a phenonium ion. Furthermore, the stereocontrolled formal synthesis of pamamycin 607 was achieved based on the ether-ring transformation.

Symmetrical σ-bridged ethylenebenzenium (phenonium) ions were proposed by Cram to explain the stereochemical results in solvolyses of optically active *threo*- and *erythro*-3-aryl-2-butyltosylates.[1] Recently, as an application of this ion to synthetic organic chemistry, we reported the solvolytic lactonization of methyl 4-aryl-5-tosyloxyalkanoates via the formation of a phenonium ion and the sequential attack of the internal ester group on the ion.[2] The chemistry of a phenonium ion can also be applied to lactone-ring transformation. Treatment of δ-lactone **1** with $TsOH{\cdot}H_2O$ in CH_3NO_2 at 70°C gives γ-lactone **2** in high yield (Scheme 1).[3] It is noteworthy that the benzylic asymmetric center on the ring can be stereospecifically transferred to a side chain in this ring transformation. As an extension of the chemistry, we report here a stereospecific ring transformation of tetrahydropyrans into tetrahydrofurans via a phenonium ion, as shown in Scheme 1, which would be applicable to the syntheses of natural products containing 2,5-disubstituted tetrahydrofurans as polyether antibiotics.[4]

Di- and tri-substituted pyrans **6**, **7**, **9**, **11**, **12** and **15** were selected as substrates of ring transformation and synthesized from *trans*-δ-lactone **1** or *cis*-δ-lactone **3** (Scheme 2). After DIBALH reduction of **1** and **3**, treatment of the corresponding lactol **4** and **5** with Et_3SiH and $BF_3{\cdot}Et_2O$ gave **6**[5] and **7**[5] in excellent yield.

The ^1H NMR spectrum of **7** showed that its stable structure has the aryl group at an axial position.[6] The coupling constants between benzyl proton and its three vicinal protons are all ca. 4 Hz. Furthermore, two proton peaks at an *ortho* position on the benzene ring of **7** appeared at a lower magnetic field (ca. 0.2 or 0.3 ppm) than those of **6**. Molecular mechanics calculation (MM2) showed that the chair conformer with an axial aryl group was ca. 0.9 kcal/mol more stable than that with an equatorial aryl group.[7]



Scheme 1. *Reagents and conditions*: (a) $TsOH{\cdot}H_2O$, CH_3NO_2, 70°C.

Keywords: phenonium ion; stereospecific ether-ring transformation; tetrahydrofuran; pamamycin 607.

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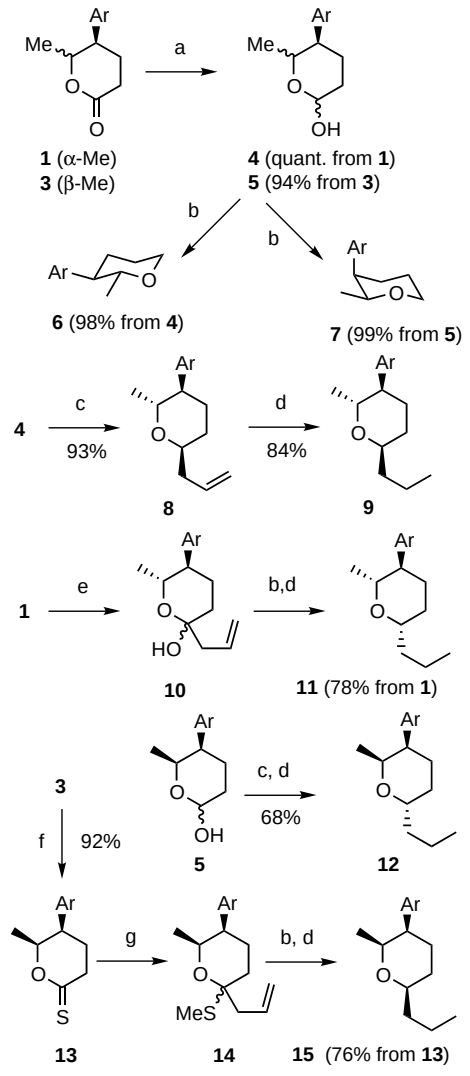
PII: S0040-4039(02)01009-2

Scheme 2



Scheme 2. *Reagents and conditions*: (a) DIBALH, toluene, −78°C; (b) Et_3SiH, $BF_3{\cdot}Et_2O$, CH_3CN, −30°C; (c) $CH_2{=}CHCH_2Si(CH_3)_3$, $BF_3{\cdot}Et_2O$, CH_2Cl_2; (d) 20% $Pd(OH)_2$–C, H_2, AcOEt; (e) $CH_2{=}CHCH_2MgBr$, THF, −50°C; (f) Lawesson's reagent, toluene, reflux; (g) (i) $CH_2{=}CHCH_2MgBr$, THF, −78°C, (ii) CH_3I. Ar = 3,4-dimethoxyphenyl.

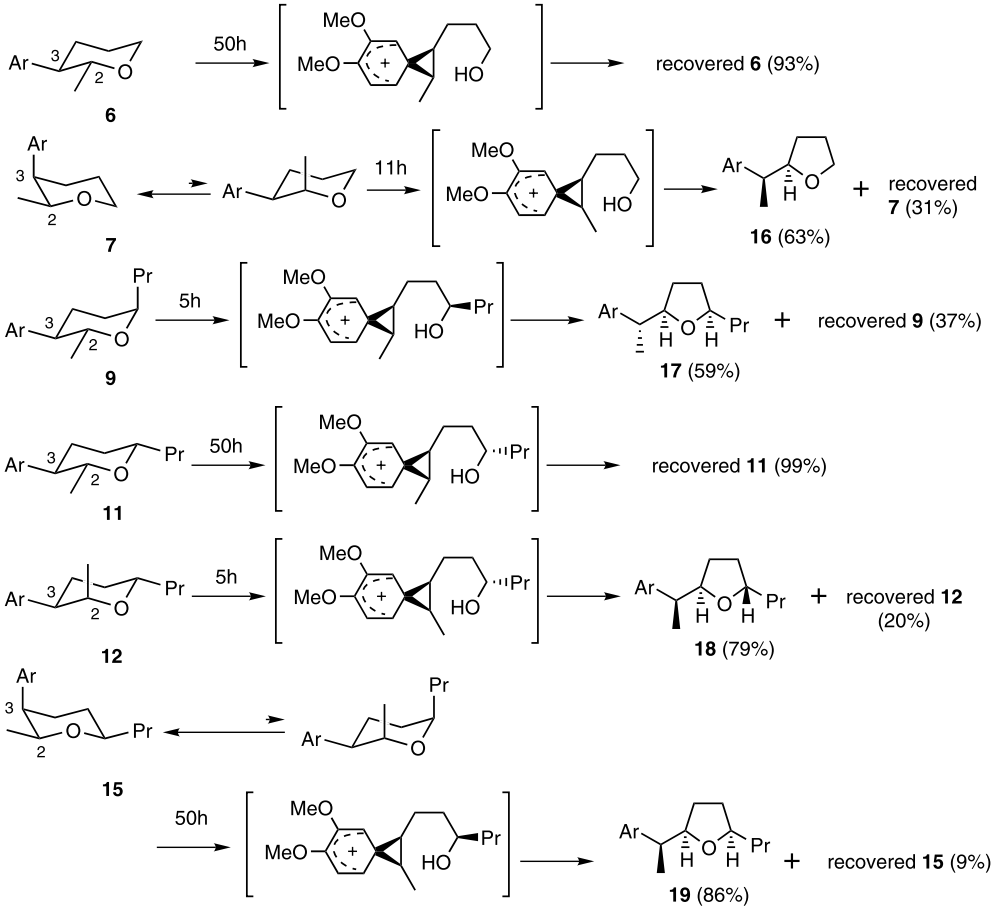
When anomeric substitution of lactol **4** with allyltrimethylsilane was carried out according to Kishi's method, *anti*-alkylated pyran **8** was stereoselectively obtained.[8] Furthermore, hydrogenation of **8** afforded the desired pyran **9**.[5] On the other hand, treatment of **1** with allylmagnesium bromide in THF at −50°C produced hemiacetal **10**, which was subjected to reduction with Et_3SiH and the subsequent hydrogenation to afford *syn*-alkylated pyran **11**[5] stereoselectively.[8]

Compound **12**[5] was prepared from **5** by the same procedure as that used for the conversion of **4** into **9**. Compound **3** was treated with Lawesson's reagent in refluxing toluene to give thiolactone **13** in 92% yield,[9,10] which was successfully converted into thioacetal **14** by allylation followed by methylation in situ. Reduction of **14** with Et_3SiH and $BF_3{\cdot}Et_2O$ proceeded stereoselectively and the resulting *syn*-allylated compound was hydrogenated to give **15** in high yield. The ^1H NMR spectrum of **15**[5] showed that its aryl group took an axial position similar to that of **7**. The total energetic difference (ca. 4.6 kcal/mol) between the stable and unstable chair conformations of **15** was found by MM2 calculation to be considerably larger than that of **7** (ca. 0.9 kcal/mol).[7] The result can be rationalized by considering the steric repulsion between axial methyl and propyl groups in the unstable chair conformation of **15**.

Ether-ring transformation of tetrahydropyrans **6**, **7**, **9**, **11**, **12** and **15** was carried out upon treatment with CF_3COOH at 70°C (Scheme 3).[11] Tetrahydropyrans **6** and **11**, which had no axial substituents, were not converted into furans under the conditions. This might be due to the overwhelming stability of the pyrans relative to the corresponding furans. On the other hand, substrates **7**, **9**, **12** and **15**, which had an axial substituent, undertook ether-ring transformation to give the corresponding tetrahydrofurans **16**–**19**[5] along with recovered substrates. Furthermore, treatment of isolated **17**–**19** with CF_3COOH at 70°C gave pyrans **9**, **12** and **15** along with recovered furans (Scheme 4). The ratio between pyrans and furans was consistent with that in the conversion of pyrans into furans. The fact that the reversible ring transformation proceeded stereospecifically can be rationalized by considering the presence of a phenonium ion as an intermediate.

Interestingly, the ring transformation of pyrans **7** and **15** having an axial aryl group proceeded more slowly than that of **9** and **12**. This finding also suggests the presence of a phenonium ion as an intermediate. An axial aryl group in the stable conformations of **7** and **15** is not antiperiplanar to a C_2–O bond. Thus, **7** and **15** should be converted into the corresponding phenonium ion via a less-stable conformation in which the phenyl group takes an equatorial position. The fact that the ring transformation of **15** was particularly slow can be rationalized by considering the remarkable energetic difference between two chair conformations of **15** obtained by molecular mechanics calculation.

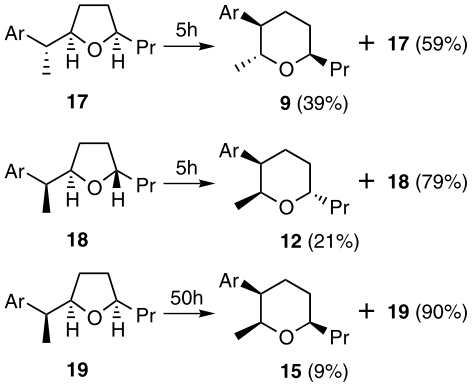
As shown above, anomeric substitution of lactol having a six-membered ring developed by Kishi et al. proceeds with high stereoselectivity to give 2,6-disubstituted tetrahydropyran.[8] However, when the procedure is applied to lactol having a five-membered ring, its stereoselectivity is not always satisfactory.[12] Consequently, our newly developed ether-ring transformation of 2,6-disubstituted pyrans into 2,5-disubstituted furans via a phenonium ion should provide us with a new stereoselective synthetic route of natural products containing 2,5-disubstituted tetrahydrofuran. In order to clarify this expectation, we carried out a synthetic study of pamamycin 607 (Scheme 5).[13,14] Compound



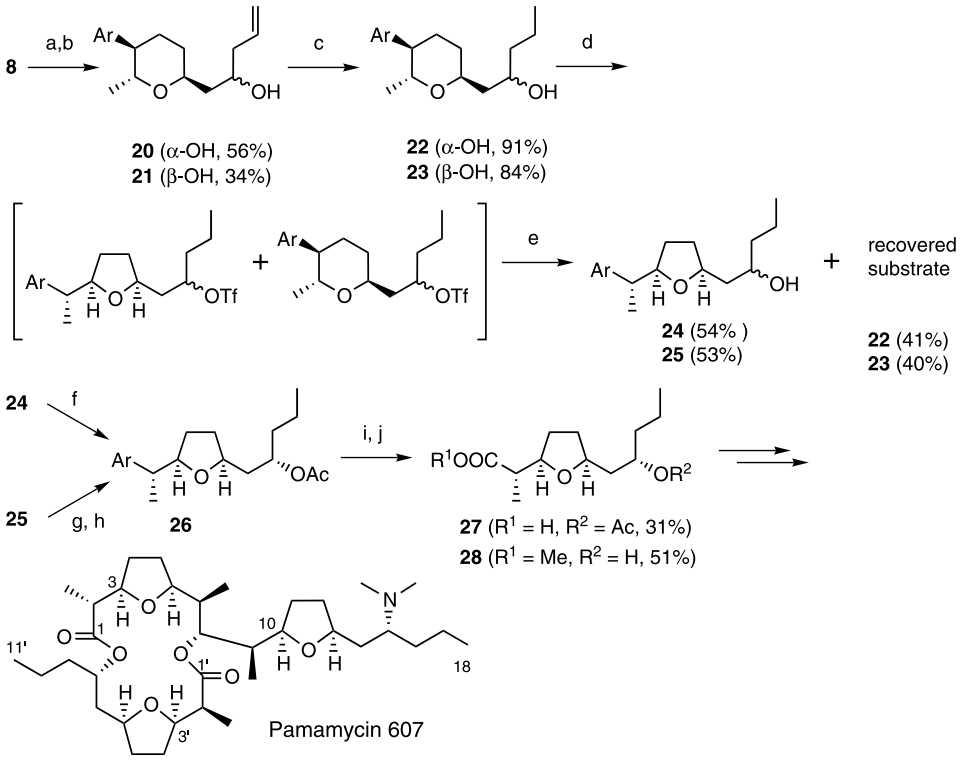
Scheme 3. *Reagents and conditions*: CF_3COOH, 70°C. Ar = 3,4-dimethoxyphenyl.

8 was subjected to oxidative cleavage of a double bond with $OsO_4/NaIO_4$ to give an aldehyde compound, which was converted into two separable alcohols **20** and **21** upon treatment with allyl Grignard reagent in the presence of $ZnCl_2$. These compounds were hydrogenated to give the corresponding alcohols **22** and **23**. The ether-ring transformation of **22** and **23** followed by alkaline hydrolysis afforded tetrahydrofurans **24** and **25** along with recovered substrates. Furan **24** was subjected to conventional acetylation to afford **26**, while another furan **25** was also converted into **26** through mesylation and subsequent substitution with CH_3COOCs. Acetate **26** was subjected to oxidative decomposition of the aromatic ring to afford carboxylate **27**.[15] Finally, **27** was successfully converted into **28**[5] through a sequence of esterification with CH_2N_2 and alkaline hydrolysis. Compound **28** corresponds to the C1′–C11′ moiety of pamamycin 607 and has already been converted into pamamycin 607 by Lee et al.[14a] The spectroscopic data of the obtained **28** are in agreement with reported data.[14a]

In conclusion, we have developed a stereospecific ring transformation of tetrahydropyran into tetrahydrofuran via a phenonium ion. The efficiency of this method was demonstrated by its application to the formal synthesis of pamamycin 607. Further application of this reaction is in progress.



Scheme 4. *Reagents and conditions*: CF_3COOH, 70°C. Ar = 3,4-dimethoxyphenyl.



Scheme 5. *Reagents and conditions*: (a) OsO_4, $NaIO_4$, *t*-BuOH, H_2O, Et_2O; (b) $CH_2CH{=}CH_2MgBr$, $ZnCl_2$, THF, −78°C; (c) 5% Pd–C, H_2, MeOH; (d) CF_3COOH, 70°C; (e) K_2CO_3, MeOH; (f) Ac_2O, DMAP, Py; (g) MsCl, DMAP, Et_3N; (h) CH_3COOCs, DMF; (i) $RuCl_3{\cdot}nH_2O$ (cat.), $NaIO_4$, CCl_4, CH_3CN, H_2O; (j) (1) CH_2N_2, Et_2O, (2) K_2CO_3, MeOH. Ar = 3,4-dimethoxyphenyl. Tf = $COCF_3$.

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5. All new compounds could be identified by spectroscopic data. For representative compounds, **6** (colorless oil): IR (neat) 2936, 1593 cm^{-1}; EI-MS *m*/*z* 236 (M^+), 164; HR-MS *m*/*z* 236.1419 (calcd for $C_{14}H_{20}O_3$: 236.1411); ^1H NMR (270 MHz, $CDCl_3$) δ 6.80 (1H, d, J = 8.0 Hz), 6.71 (1H, dd, J = 2.0, 8.0 Hz), 6.67 (1H, d, J = 2.0 Hz), 4.04 (1H, dt, J = 3.0, 11.2 Hz), 3.88 (3H, s), 3.86 (3H, s), 3.55 (1H, dt, J = 3.0, 11.2 Hz), 3.48 (1H, dq, J = 6.3, 9.9 Hz), 2.33 (1H, ddd, J = 3.6, 9.9, 11.2 Hz), 2.00–1.90 (1H, m), 1.83–1.57 (3H, m), 0.98 (3H, d, J = 6.3 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 148.70 (s), 147.41 (s), 136.33 (s), 119.38 (d), 119.38 (d), 111.13 (d), 110.79 (d), 78.27 (d), 68.23 (t), 55.71 (q, ×2), 55.01 (d), 32.21 (t), 26.45 (t), 19.96 (q). **7** (colorless oil): IR (neat) 2936, 1589 cm^{-1}; EI-MS *m*/*z* 236 (M^+), 164; HR-MS *m*/*z* 236.1396 (calcd for $C_{14}H_{20}O_3$: 236.1411); ^1H NMR (270 MHz, $CDCl_3$) δ 7.01 (1H, d, J = 2.0 Hz), 6.94 (1H, dd, J = 8.0, 2.0 Hz), 6.81 (1H, d, J = 8.0 Hz), 4.10–3.98 (1H, m), 3.96–3.86 (1H, qd, J = 6.6, 3.6 Hz), 3.88 (3H, s), 3.87 (3H, s), 3.68–3.56 (1H, m), 2.78 (1H, td, J = 4.6, 3.6 Hz), 2.02–1.78 (3H, m), 1.48–1.36 (1H, m), 1.06 (3H, d, J = 6.6 Hz). ^{13}C NMR (68 MHz, $CDCl_3$) δ 148.36 (s), 147.25 (s), 135.32 (s), 121.28 (d), 112.80 (d), 110.79 (d), 75.58 (d), 66.62 (t), 55.85 (q), 55.78 (q), 44.23 (d), 29.17 (t), 22.18 (t), 17.75 (q). **9** (colorless oil): IR (neat) 1593, 1518 cm^{-1}; EI-MS *m*/*z* 278 (M^+), 164; HR-MS *m*/*z* 278.1877 (calcd for $C_{17}H_{26}O_3$: 278.1881); ^1H NMR (270 MHz, C_6D_6) δ 6.76–6.60 (3H, m), 3.98–3.85 (2H, m), 3.47 (3H, s), 3.44 (3H, s), 2.40–2.30 (1H, m), 2.04–1.70 (4H, m), 1.60–1.20 (4H, m), 1.18 (3H, d, J = 5.9 Hz), 0.96 (3H, t, J = 7.3 Hz); ^{13}C NMR (68 MHz, C_6D_6) δ 150.17 (s), 148.85 (s), 137.53 (s), 119.96 (d), 112.73 (d, ×2), 71.69 (d), 70.19 (d), 55.77 (q), 55.73 (q), 49.66 (d), 33.36 (t), 28.97 (t), 27.73 (t), 20.42 (q), 19.69 (t), 14.32 (q). **11** (colorless oil): IR (neat) 1593, 1518 cm^{-1}; EI-MS *m*/*z* 278 (M^+), 164; HR-MS *m*/*z* 278.1857 (calcd for $C_{17}H_{26}O_3$: 278.1881); ^1H NMR (270 MHz, $CDCl_3$) δ 6.80 (1H, d, J = 8.1 Hz), 6.70 (1H, dd, J = 8.1, 1.9 Hz), 6.67 (1H, d, J = 1.9 Hz), 3.87 (3H, s), 3.85 (3H, s), 3.57–3.37 (2H, m), 2.28 (1H, ddd, J = 11.9, 9.7, 3.8 Hz), 2.00–1.88 (1H, m), 1.82–1.62 (2H, m), 1.62–1.20 (5H, m), 0.99 (3H, d, J = 6.3 Hz), 0.94 (3H, t, J = 7.3 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 148.71 (s), 147.38 (s),

136.48 (s), 119.45 (d), 111.14 (d), 110.82 (d), 78.10 (d), 77.48 (d), 55.73 (q, ×2), 49.89 (d), 38.49 (t), 32.51 (t), 31.90 (t), 20.04 (q), 18.79 (t), 14.06 (q). **12** (white crystals): EI-MS m/z 278 (M^+), 164, 149; HR-MS m/z 278.1884 (calcd for $C_{17}H_{26}O_3$: 278.1881); ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.81 (1H, d, $J=8.5$ Hz), 6.74–6.69 (2H, m), 4.23 (1H, quintet, $J=6.8$ Hz), 3.86 (3H, s), 3.85 (3H, s), 3.69–3.58 (1H, m), 3.08 (1H, ddd, $J=12.4$, 6.8, 3.4 Hz), 2.13–1.95 (1H, m), 1.86–1.71 (2H, m), 1.55–1.30 (5H, m), 0.98 (3H, t, $J=6.8$ Hz), 0.93 (3H, t, $J=6.8$ Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 148.69 (s), 147.41 (s), 135.35 (s), 119.30 (d), 111.05 (d, ×2), 73.81 (d), 67.89 (d), 55.80 (q), 55.77 (q), 44.60 (d), 38.39 (t), 32.08 (t), 22.58 (t), 18.71 (t), 14.05 (q), 12.26 (q). **15** (colorless oil): EI-MS m/z 278 (M^+), 164; HR-MS m/z 278.1860 (calcd for $C_{17}H_{26}O_3$: 278.1881); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.12 (1H, d, $J=1.6$ Hz), 6.96 (1H, dd, $J=8.2$, 1.6 Hz), 6.79 (1H, d, $J=8.2$ Hz), 3.88 (3H, s), 3.86 (3H, s), 3.90–3.78 (1H, m), 3.51–3.40 (1H, m), 2.61 (1H, br), 2.00 (1H, tt, $J=13.2$, 4.9 Hz), 1.80 (1H, br d, $J=13.2$ Hz), 1.73–1.30 (6H, m), 1.09 (3H, d, $J=6.6$ Hz), 0.95 (3H, t, $J=6.9$ Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 148.05 (s), 147.01 (s), 135.38 (s), 121.90 (d), 113.38 (d), 110.61 (d), 78.01 (d), 75.79 (d), 55.67 (q, ×2), 43.62 (d), 38.95 (t), 31.74 (t), 25.68 (t), 19.92 (q), 18.54 (t), 14.18 (q). **16** (colorless oil): EI-MS m/z 236 (M^+), 165; HR-MS m/z 236.1426 (calcd for $C_{14}H_{20}O_3$: 236.1411); ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.80 (3H, s), 4.00–3.64 (3H, m), 3.88 (3H, s), 3.85 (3H, s), 2.74 (1H, quintet, $J=7.0$ Hz), 2.03–1.72 (3H, m), 1.64–1.48 (1H, m), 1.26 (3H, d, $J=7.0$ Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 148.65 (s), 147.37 (s), 137.28 (s), 119.60 (d), 111.08 (d), 111.01 (d), 83.78 (d), 68.14 (t), 55.80 (q), 55.77 (q), 44.01 (d), 29.54 (t), 25.81 (t), 18.54 (q). **17** (colorless oil): EI-MS m/z 278 (M^+), 165; HR-MS m/z 278.1869 (calcd for $C_{17}H_{26}O_3$: 278.1881); ^{1}H NMR (270 MHz, C_6D_6) δ 6.79–6.70 (2H, m), 6.63 (1H, d, $J=7.9$ Hz), 3.91 (1H, q, $J=7.3$ Hz), 3.79 (1H, quintet, $J=6.9$ Hz), 3.48 (3H, s), 3.44 (3H, s), 2.74 (1H, quintet, $J=7.3$ Hz), 1.70–1.16 (8H, m), 1.51 (3H, d, $J=7.3$ Hz), 0.94 (3H, t, $J=6.9$ Hz); ^{13}C NMR (68 MHz, C_6D_6) δ 150.08 (s), 148.84 (s), 137.95 (s), 119.97 (d), 112.66 (d), 112.55 (d), 84.17 (d), 79.46 (d), 55.72 (q), 55.65 (q), 45.91 (d), 38.82 (t), 31.44 (t), 29.99 (t), 19.96 (t), 19.35 (q), 14.47 (q). 18 (colorless oil): EI-MS m/z 278 (M^+), 165; HR-MS m/z 278.1877 (calcd for $C_{17}H_{26}O_3$: 278.1881); ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.86–6.74 (3H, m), 4.14–4.03 (1H, m), 3.87 (3H, s), 3.85 (3H, s), 3.87–3.75 (1H, m), 2.79 (1H, quintet, $J=6.9$ Hz), 1.95–1.82 (2H, m), 1.72–1.30 (6H, m), 1.27 (3H, 6.9 Hz), 0.89 (3H, t, $J=6.9$ Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 148.66 (s), 147.43 (s), 137.07 (s), 120.01 (d), 111.76 (d), 111.08 (d), 82.77 (d), 79.11 (d), 55.90 (q), 55.83 (q), 43.96 (d), 38.09 (t), 32.16 (t), 29.37 (t), 19.41 (t), 17.60 (q), 14.13 (q). **19** (colorless oil): EI-MS m/z 278 (M^+), 165; HR-MS m/z 278.1906 (calcd for $C_{17}H_{26}O_3$: 278.1881); ^{1}H NMR (270 MHz, C_6D_6) δ 6.89 (1H, d, $J=2.0$ Hz), 6.83 (1H, dd, $J=8.2$ Hz), 6.81 (1H, dd, $J=8.2$, 2.0 Hz), 3.91 (1H, q, $J=5.9$ Hz), 3.70 (1H, quintet, $J=6.6$ Hz), 3.53 (3H, s), 3.44 (3H, s), 2.81 (1H, quintet, $J=6.9$ Hz), 1.68–1.22 (7H, m), 1.34 (3H, d, $J=6.9$ Hz), 1.20–1.08 (1H, m), 0.88 (3H, t, $J=6.9$ Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 148.40 (s), 147.32 (s), 136.94 (s), 119.85 (d), 111.69 (d), 110.81 (d), 83.51 (d), 79.07 (d), 55.80 (q), 55.69 (q), 44.00 (d), 38.28 (t), 31.05 (t), 28.39 (t), 19.35 (t), 17.34 (q), 14.20 (q). **28** (colorless oil): EI-MS m/z 226 (M^+-H_2O), 157; HR-MS m/z 226.1569 (calcd for $C_{13}H_{22}O_3$: 226.1568); ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.20–3.94 (3H, m), 3.70 (3H, s), 2.54 (1H, quintet, $J=6.9$ Hz), 2.10–1.90 (2H, m), 1.81–1.54 (5H, m), 1.21 (3H, d, $J=6.9$ Hz), 1.13 (3H, d, $J=6.9$ Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.52 (q), 81.06 (d), 77.26 (d), 65.16 (d), 51.70 (q), 45.28 (d), 42.61 (t), 30.50 (t), 28.82 (t), 23.16 (q), 13.52 (q).

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11. A solution of pyran (100 mg) in CF_3COOH (5 ml) was stirred at 70°C.
12. For example, anomeric substitution of the lactol compound, which was obtained by DIBALH reduction of **2**, did not proceed stereoselectively to give a ca. 1:1 mixture of two diastereomeric 2,5-disubstituted tetrahydrofurans.
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